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10.5 APPROACHES TO DETECTING MISLABELLED CHEESES

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ABSTRACT

Rheological behavior, melting characteristics, and examination of microstructure can be used to identify mislabelled cheeses. Differential scanning calorimetry (DSC) was used in conjunction with scanning electron microscopy (SEM) to differentiate between natural and imitation Mozzarella cheeses made with calcium caseinate. DSC curves revealed that the enthalpy of the milkfat melting transition at 18°C decreased with increasing caseinate concentration; caseinate addition apparently affected fat crystallization. SEM showed that the lipids had agglomerated in the imitation samples whereas there was a uniform dispersion of fat droplets within the protein matrix of the natural cheese. Measurement of dynamic shear moduli with a mechanical spectrometer showed that both elastic and viscous components of the shear modulus varied with the percentage of added caseinate. This technique was applied to distinguish between Cheddar and Cheshire cheeses. Both of these varieties followed the Arrhenius equation; the energy of activation obtained varied with age and variety of cheese. Objective characterizations such as these can assume great importance in identification of cheeses.

1 INTRODUCTION

Gas chromatographic analysis of fatty acids and triglycerides has long been used to detect misrepresented dairy products, especially those in which inexpensive vegetable fat has been used as a substitute for milkfat [1]. Standard analytical techniques are not always sufficient, however, when other types of improper labelling are to be investigated. For instance, Cheddar cheese may be mislabelled as Cheshire, which commands a much higher retail price in the US. Fatty acid analysis is not useful when distinguishing these two varieties since they both contain milkfat, and their compositional analyses are virtually the same [2]. Cheddar and Cheshire are normally sold after months of aging, resulting in large amounts of proteolytic breakdown, which precludes the use of electrophoresis as a means of distinguishing the two.

Another example is misrepresentation of imitation Mozzarella cheese as genuine. The Standards of Identity for Mozzarella cheese in the US do not allow for the use of added caseinates [3], which, if present in the milk at a concentration of 1%, would increase the yield by up to 24% [4]. The economic savings that may result from substituting genuine Mozzarella with an imitation product may tempt an unscrupulous manufacturer, particularly since the two products are compositionally similar.

Fortunately, certain analytical techniques can be used to detect mislabelling of cheese. The melting properties of the fat in a sample can be examined by DSC, which can detect changes caused by the addition of an ingredient such as calcium caseinate. Cheshire cheese, which is manufactured to keep the curd particles separate, and Cheddar cheese, which is cheddared in order to spread out the curd particles and mat them together [5], have textural differences which can be distinguished by rheological techniques. Furthermore, the microstructure of cheese can be observed by SEM. These analytical methods provide the investigator with additional tools for correctly identifying suspect cheeses.

2 MATERIALS AND METHODS

Low moisture part skim Mozzarella cheeses were made from locally obtained fresh raw milk according to the procedure described by Kosikowski [6]. These samples were identified as natural Mozzarella containing 0% added calcium caseinate. Calcium caseinate powder (New Zealand Milk Products, Inc.[1], Petaluma, CA) was stirred into the milk of the imitation cheeses to a concentration of 1 or 2% by weight. Samples were vacuum-packaged and stored at 4°C. Samples of 20-week-old Cheshire cheese and 60-week-old Cheddar cheese were manufactured in England, purchased locally, and stored at 4°C. A 20-week-old English Cheddar was not obtained since this variety is aged much longer before export.

Thermal behavior was examined by DSC using a Perkin-Elmer DSC-2 (Perkin-Elmer Co., Norwalk, CT). Samples weighing 2-6 mg were sealed in volatile sample pans, placed in the instrument, and heated at 10°C/min with nitrogen as the purge gas. Temperature-treated samples were held at 60°C for 5 min, cooled at 10°C/min to -40°C, and held at that temperature for 5 min prior to heating. Samples not designated as temperature treated were removed from refrigerated storage, weighed and sealed in volatile sample pans, and immediately heated from 5 to 25°C.

Viscoelastic properties were determined with a Rheometrics Dynamic Analyzer 700 (Rheometrics, Inc., Piscataway, NJ), using a 0-200 g-cm torque transducer and parallel plates with a diameter of 2.50 cm. A cork borer was used to obtain a sample disk with a diameter of 2.5 cm and a height of 4 mm. Cyanoacrylate bonding agent was used to glue the sample to the plates to prevent slippage. Samples were analyzed at 20°C unless otherwise noted. The data included the two components of the shear complex modulus G^*: the elastic (shear storage modulus) component G' and the viscous (shear loss modulus) component G''. Both were measured in dyn/cm^2. The complex viscosity η^* and the frequency ω (in rad/s) were also measured. These parameters are related as follows:

$$G^* = \sqrt{(G')^2 + (G'')^2}$$

$$\eta^* = \frac{G^*}{\omega}$$

[1] *Use of brand name or firm name does not constitute endorsement by the US Department of Agriculture over others of a similar nature not mentioned.*

Samples were prepared for SEM by procedures described by Kalab [7]. Cubes measuring 1-2 mm on a side were removed from the interior of each cheese and fixed with 3.5% glutaraldehyde in 0.05% sodium cacodylate (pH 6.6) at 4°C overnight. After three rinses with the cacodylate, the sample was postfixed with 2% osmium tetroxide in cacodylate at 25°C for 2 h. After three more cacodylate rinses, the sample was dehydrated in a graded ethanol series, freeze-fractured, critical-point dried, mounted, given a sputter coat of gold, and examined with a JEOL JSM-840A SEM (JEOL, Inc., Peabody, MA) operating at 10 kV.

3 RESULTS AND DISCUSSION

The thermal history of a fat sample is erased when it is held above its melting point; cooling it quickly and holding it below the point where melting begins allows the fat to crystallize in a fairly uniform manner [8]. Treating Mozzarella in this manner in a DSC produces a curve such as the one in Figure 1 [9]. Endothermic transitions corresponding to the melting of milkfat are found at temperatures above the 0°C water peak. All of the natural and imitation Mozzarellas exhibited similar DSC curves. Different results were obtained when the samples were not temperature treated. When the samples were removed from 4°C storage and immediately scanned from

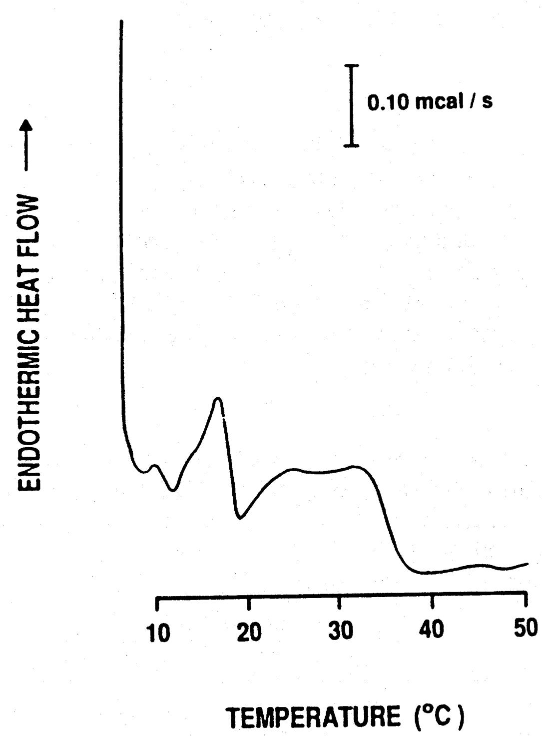

Figure 1: Portion of DSC curve of 7.4 mg of temperature-treated natural Mozzarella. Sample was held at 60°C for 5 min, cooled to -40°C and held for 5 min, and heated.

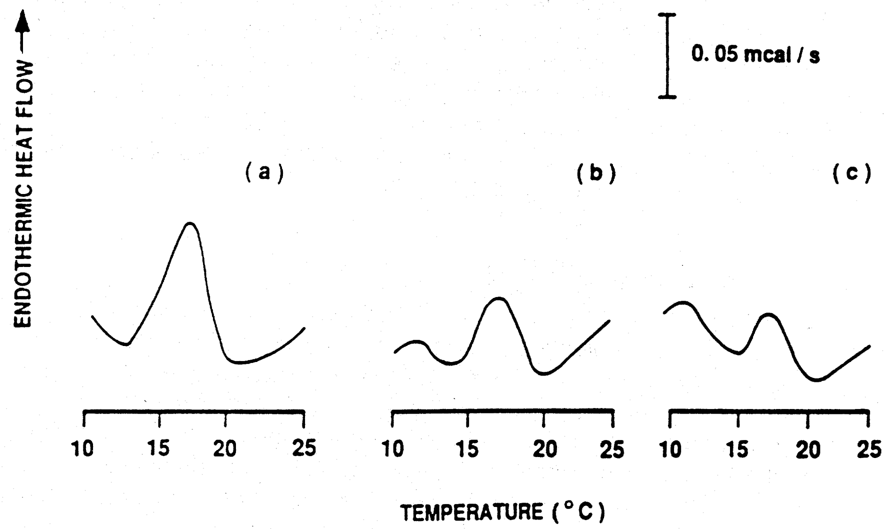

Figure 2: a, b, c – Portions of DSC curves, without temperature treatment, of Mozzarella made with 0, 1, and 2% added calcium caseinate, respectively. Each sample weighed 4.6 mg.

5 to 25°C, there were variations in the thermal transitions around 16-18°C depending on the caseinate concentration (Figure 2). These differences were quantitated by comparing the enthalpies of these peaks. The enthalpy (ΔH) of a transition is equal to its peak area in mcal divided by mg sample. To account for differences in fat content, the weight was considered to be that of the fat in the sample, or % fat times mg sample. Table 1 shows that the ΔH of the 18°C transition among Mozzarellas with no temperature treatment decreased with increasing caseinate concentration. The melting points of the lipids did not vary.

Table 1: Enthalpies (with standard deviations) of 18°C transitions in natural and imitation Mozzarellas from two sample preparation runs

Added calcium caseinate (%)	Run 1 (n = 5) ΔH (cal/g fat)		Run 2 (n = 7) ΔH (cal/g fat)	
	Ave.	SD	Ave.	SD
0	2.44	0.51	2.69	0.60
1	1.12	0.38	1.09	0.29
2	0.59	0.09	0.55	0.07

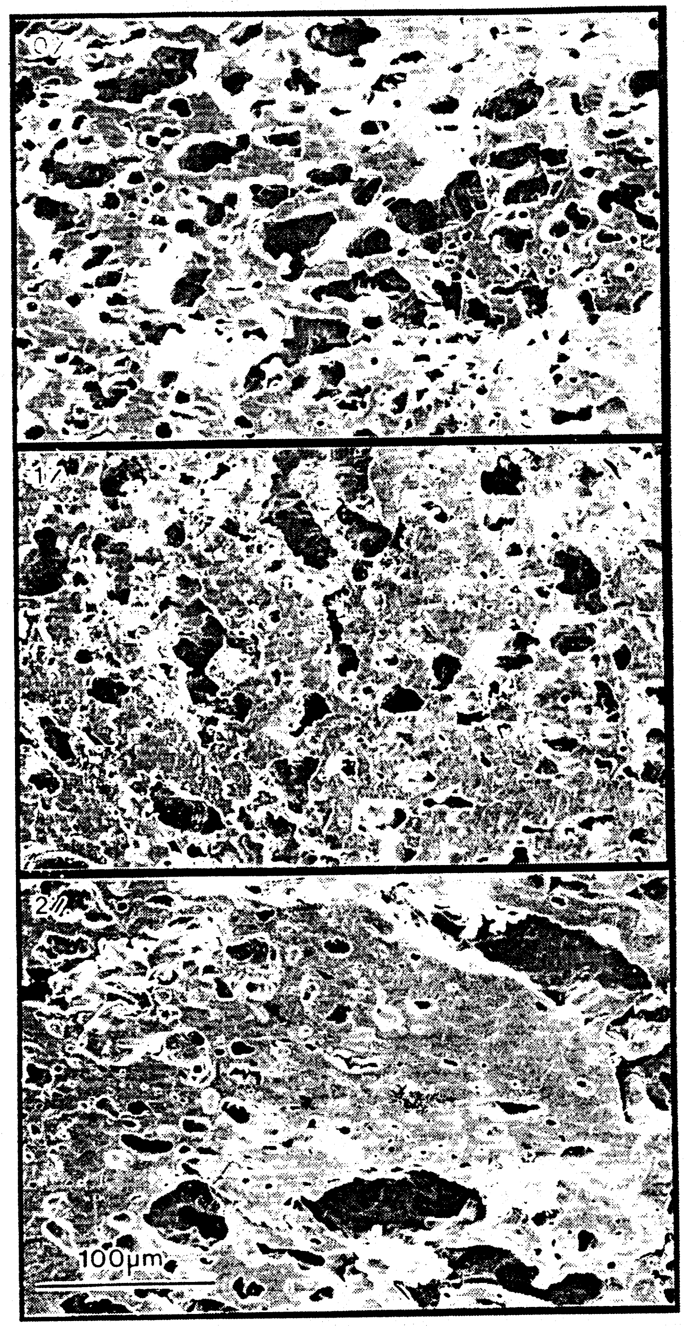

Figure 3: *Scanning electron micrographs of Mozzarellas made with 0, 1, and 2% added calcium caseinate, respectively. Dark areas indicate sites occupied by fat globules.*

The DSC results are explained by comparing the microstructures of natural and imitation Mozzarellas. Fat globules were uniformly dispersed throughout the protein network of natural Mozzarella, but were flattened, randomly dispersed, and often agglomerated into larger bodies in Mozzarella containing 2% added calcium caseinate (Figure 3). The matrix in the 2% added caseinate cheese had zones in which there were large areas of protein without lipid and other areas where fat was plentiful. The 1% added caseinate Mozzarella showed a mixture of the effects observed in the natural and 2% added caseinate cheeses. The change in the characteristics of fat globules in imitation Mozzarella has been observed previously [10]. The similarities in the DSC curves suggest that temperature treatment of either type of Mozzarella causes both types to develop a more uniform dispersion of fat. The fat globule dispersion is apparently unaltered when the sample is not temperature treated, allowing differences in thermal behavior to be observed. The emulsifying properties of the added caseinate apparently prevent some of the fat from crystallizing during refrigerator storage, resulting in a smaller thermal transition when the sample is heated.

Addition of calcium caseinate had an effect on the rheological properties of the Mozzarellas [11]. The viscosity of the cheese containing 1% added caseinate was 30% higher than that of the natural Mozzarella, and the viscosity of the 2% added caseinate cheese was 50% higher. At 0.5% strain the 1% caseinate cheese had larger G' and G" values than the natural cheese, but the 2% added caseinate Mozzarella had a lower G' value (Table 2).

Table 2: Shear moduli of natural and imitation Mozzarella cheeses at 0.5% strain

Added calcium caseinate (%)	G' (dyn/cm^2)	G" (dyn/cm^2)
0	$2.27 \times 10^5\ \omega^{0.17}$	$1.03 \times 10^5\ \omega^{0.19}$
1	$5.92 \times 10^5\ \omega^{0.20}$	$1.983 \times 10^5\ \omega^{0.14}$
2	$1.59 \times 10^5\ \omega^{0.21}$	$1.98 \times 10^5\ \omega^{0.16}$

Cheddar and Cheshire cheese cannot be distinguished from each other by SEM or DSC. However, rheological measurements demonstrated clear differences between the cheeses [12]. Values of η^* for the cheeses at a strain of 2.5% and a ω of 1.0 rad/s were obtained at various temperatures. Table 3 shows the decrease in log η^* with increasing temperature.

With each cheese, a plot of η^* versus reciprocal of absolute temperature (1/T) produced a straight line which followed the Arrhenius equation:

$$\eta^* = A_{visc} \exp(-E_{visc}/RT)$$

where A_{visc} is the pre-exponential factor, E_{visc} is the activation energy, and R is the gas constant (1.987 cal/°C mol). When η^* is converted to log 10, E_{visc} is equal to the slope of the line multiplied by 2.303R. The Arrhenius equations and activation energies of the samples are shown in Table 4.

Table 3: Values of log of complex viscosity at various temperatures for the Cheshire and Cheddar cheeses

Temperature (°C)	20-week Cheshire	60-week Cheshire	60-week Cheddar
		log η^*	
20	6.05	5.94	6.19
25	5.90	5.71	5.74
30	5.64	5.50	5.40
35	5.24	5.23	5.00
40	4.91	4.96	4.60

Table 4: Arrhenius equations and activation energies (in cal/mol), for the Cheshire and Cheddar cheeses

Sample	log η^*	E_{visc}
20-week Cheshire	5331/T - 12.05	24400
60-week Cheshire	4442/T - 9.20	20250
60-week Cheddar	7156/T - 18.24	32750

The η^* and E_{visc} of the Cheshire decreased approximately 20% from 20 to 60 week since the body of the cheese was breaking down. Thebody of the Cheddar broke down less easily than that of the Cheshire, as evidenced by the higher E_{visc} of the Cheddar.

4 CONCLUSIONS

The thermal and rheological properties of cheese vary from one variety to the next, and can be sensitive to changes in processing. Use of DSC and mechanical spectroscopy may therefore enable an investigator to detect certain types of mislabelling. In addition, changes in microstructure can be observed by SEM. These analytical techniques can be used to aid in distinguishing among cheese varieties when more conventional methods fail.

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